

New organic photochromic materials and selected applications

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Materials

ABSTRACT

Purpose: The aim of this work is to perform the review of the recent most important results of experimental and theoretical investigations connected with the photochromic materials and their selected applications.

Design/methodology/approach: The recent achievements in the field of designing and preparation methods of organic photochromic materials and devices operating as three-dimensional optical data storage.

Findings: We pointed out the important role that play the photochromic effect in organic materials and which can be used as the above mentioned devices.

Research limitations/implications: The main disadvantage of organic materials are reported to be to short their lives and weak resistivity to the moist but the improvements are advancing.

Originality/value: Our review concerns the most recent findings in this area. We also show some recent examples of photochromic organic material application in 3D memory devices.

Keywords: Photochromism; Organic materials; Optoelectronics

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1. Introduction

Photochromism is defined as a reversible transformation in a chemical species between two forms having different absorption spectra by photoirradiation. It is simply a *light-induced reversible change of color*. It has become a common name because many people wear photochromic spectacles that darken in the sun and recover their transparency in diffuse light. The first commercial glasses were made of glass lenses impregnated with inorganic (mainly silver) salts. Let us start with the photochromic effect in inorganic materials. We have carried out the studies on photochromic absorption in sillenite single crystals doped mainly with transient metal elements (Mn, Cr and Co) [1].

The photochromic effect is a reversible process of absorption changes in some materials induced by illumination. The changes can be removed and the absorption can be brought into its initial value by means of illumination as well as by annealing. In papers [1,2] the special attention has been devoted to the single crystals such as Bi₁₂GeO₂₀ (BGO), Bi₁₂SiO₂₀ (BSO) and BTPbO doped with transition or rare earth metals. In these papers we describe the measurement methods and instrumentation connected with this effect and the selected basic absorption spectra of the investigated single crystals enabling to understand some features of the photochromic effect occurring in these crystals. The attached in these papers some selected curves provide the valuable information concerning the physical phenomena involved in coloring and decoloring processes in these single

crystals. We found that in the case of BGO and BSO single crystals the doping elements of transient metal replace germanium (silicon) atoms. The photochromic effect should be connected with the change in their charge state by one electron i.e. $\text{Mn}^{+4} \rightarrow \text{Mn}^{+5}$ and $\text{Cr}^{+3} \rightarrow \text{Cr}^{+4}$. The absorption in Mn^{+4} ion results in the transition of the electron to the conduction band where it is trapped in the electron trap. Before the illumination both Mn^{+4} and Mn^{+5} centers exist. After illumination almost all Mn^{+4} centers are transferred to the Mn^{+5} state. The similar model was proposed for the case of BGO:Cr, here we have $\text{Cr}^{+3} \rightarrow \text{Cr}^{+4}$ transition. In the case of BTPbO mixed crystals, the absorption bands are associated with the polaron bound to the ion localized tetrahedrally or to the analogous center Bi^{+3+h} . Some BTPbO single crystals show the so called gray spectrum. This kind of spectrum is likely to consist of many other almost identical bands located closely to each.

Now some latest achievements in investigations of photochromic effect in organic materials. In recent years, organic photochromic lenses, which are lighter and therefore more comfortable to wear despite their limited lifetime, have made an important breakthrough in the world market. The fact that some chemical species can undergo reversible photochemical reactions creates a possibility of a number applications. For example the reversible physical phenomena can be applied in optical data memory systems (photon-mode erasable optical recording media) [3], optical memories and switches, variable electrical current, ion transport through membranes, variable wettability, etc. For this purpose, organic photochromic compounds are often incorporated in polymers, liquid crystalline materials, or other matrices.

Numerous other uses have also been explored with encouraging results. In the case of optical storage memory systems, the interest of photochromic compounds is based on the fact that photon-mode recording has certain advantages over the heat-mode, regarding resolution speed of writing and multiplex recording capability [3]. Also, fatigue due to material movement is eliminated. Despite these advantages, photochromic molecules still await further practical applications. The reason is that they must fulfill many requirements such as: a) low photofatigue (can be cycled many times without loss of performance), b) storage capability (thermal stability), c) sensitivity to the diode laser (650–830 nm), d) high quantum yields and e) non destructive read-out capability. Optical memory storage devices such as compact disks (CD) and magneto-optical (MO) disks are becoming essential as audio and visual storage media as well as external computer data storage media. In these devices, a laser beam is used to record and read information. Since the laser spot can be focused to within 1 μm , higher densities and capacities can be achieved with optical memory than with conventional magnetic memory.

The data density achievable by optical memory devices is ultimately limited by the diffraction of electromagnetic waves. Present data-recording techniques have nearly attained this upper limit with commercially available CD and MO disks. Even utilizing an infinitely large objective lens with a high numerical-aperture (NA) value cannot reduce the bit data resolution distance for recording and reading to less than one-half the beam wavelength. Some improvements can be expected with application of the short-wavelength compact lasers that emit blue or green light [4]. Doubling the frequency of the laser reduces the beam spot radius by 2, thereby increasing the density by 4 (when

recorded in two dimensions). However, to increase the memory density to 100 times the current benchmark, laser diodes with output wavelengths 10 times shorter than those currently available would have to be employed. Another approach to increasing memory density is to use near-field optics [5,6].

A third approach, and one which promises to dramatically increase memory densities, is the development of photochromic materials [7,8]. These materials can undergo photon-mode recording, which is based on a photochemical reaction within the medium, as opposed to the heat-mode recording employed with the optical media currently in use. In photon-mode recording, light characteristics such as wavelength, polarization, and phase can be multiplexed to enable data storage and thus have the potential to dramatically increase the achievable memory density.

In this review we describe a method which utilizes photochromic materials to overcome the current memory density limit by introducing an additional axial dimension to the recording process [9,10]. In this method, the z or longitudinal axis is utilized in addition to the surface dimension (x - y space) of conventional optical memory. The data are thus written not on the material surface, but within the three-dimensional (3D) volume of the material. This review focuses on recent developments in bit-oriented multilayered optical memories based on photochromic materials. The photochromic materials dealt with here are all synthetic ones.

2. Brief historical survey

Fritzsche reported in 1867 [11] the bleaching of an orange-colored solution of tetracene in the daylight and the regeneration of the color in the dark. Later, ter Meer [12] found a change of color of the potassium salt of dinitroethane in the solid state (yellow in the dark; red in the daylight). In 1899, Markwald studied the reversible change of color of 2,3,4-tetrachloronaphthalen-1(4H)-one (@-TCDHN) in the solid state [13]. He believed it was a purely physical phenomenon, naming it "phototropy". Although used in that period, that term is not proper and should be avoided because it is akin to phototropism, which denotes biological phenomena (*vide infra*). Interest in photochromism was continuous but limited until the 1940–1960 period, which saw an increase of mechanistic and synthetic studies, particularly in the research groups of Hirshberg and Fischer in Israel. In 1950, Hirshberg [14] suggested the term "photochromism" [from the Greek words: *phos* (light) and *chroma* (color)] to describe the phenomenon. This is the name used today. However, it is not limited to colored compounds; it applies to systems absorbing from the far UV to the IR, and to very rapid or very slow reactions.

During the 1960s photochromism expanded in parallel with the development of physical methods (IR, NMR, X-ray, UV, time-resolved and flash spectroscopy) and organic synthesis. Photochromic glasses became available at that period and it stimulated the further research. Applications, such as the photochromic micro image (PCMI) process, which showed for example the possibility of reducing the 1245 pages of a Bible to about 6 cm^2 , attracted considerable interest. An important book was published in 1971 [15]. However, it appeared that the photodegradation of the known families of organic photochromes limited their potential for applications [16]. A revival of activity started in the 1980s, essentially because of the development of

fatigue-resistant *spirooxazine* and *chromene* derivatives. They triggered the fabrication and commercial application of photochromic ophthalmic lenses. Since then, other commercial systems have been developed, and new photochromic systems have been discovered and explored. In parallel, several books have been printed (*vide infra*); a flow of articles in scientific journals has appeared and International Symposia on Photochromism (ISOP) have been organized.

3. General definitions and concepts

3.1. Definition of photochromism

Photochromism is a reversible transformation of a chemical species induced in one or both directions by absorption of electromagnetic radiation between two forms, A and B, having different an absorption spectra (Fig. 1). The thermodynamically stable form A is transformed by irradiation into form B. The back reaction can occur thermally (*Photochromism of type T*) or photochemically (*Photochromism of type P*).

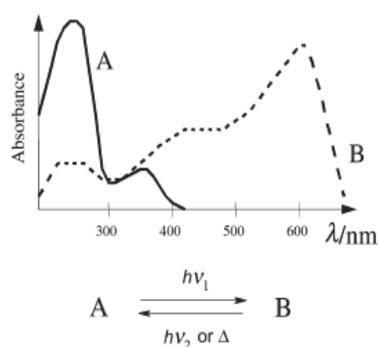


Fig. 1. Dependence of absorption on wavelength for two different photochromic materials A and B

The most prevalent organic photochromic systems involve *unimolecular* reactions: the most common photochromic molecules have a colorless or pale yellow form A and a colored form B (e.g. red or blue). This phenomenon is referred to as *positive photochromism*. Other systems are *bimolecular*, such as those involving photocycloaddition reactions. When $\lambda_{\max}(A) > \lambda_{\max}(B)$, *photochromism is negative or inverse*.

The unimolecular processes are encountered, for example, with *spiropyrans*, a family of molecules that has been studied extensively. Solid photochromic spiropyrans or solutions (in ethanol, toluene, ether, ketones, esters, etc.) are colorless or weakly colored. Upon UV irradiation, they become colored. The colored solutions fade *thermally* to their original state; in many cases, they can also be decolorized (*bleached*) by visible light. A few spiropyrans display negative photochromism. They are colored in the dark and *bleached* by UV light. Many spiropyrans are also *thermochromic* (see definition below), and spectra of the colored forms are identical to those produced photochemically.

3.2. Single-photon and two-photon models

In general, the photochromic processes involve an one-photon mechanism. B is formed from the singlet ($1A^*$) or triplet ($3A^*$) excited states or both. B, the photoproduct, may also be formed from an upper excited state populated by absorption of two photons.

Two-photon photochromism

The transition probability to populate the final state (hence to obtain the photoproduct) depends on the product of the photon irradiances $E_p(1)$ and $E_p(2)$ of the two exciting beams. It is, therefore, advantageous to utilize lasers emitting high photon irradiance, such as those generating picosecond or subpicosecond pulses. Two absorption processes may be distinguished:

- simultaneous absorption of two photons via a virtual level (Fig. 2a).
- stepwise (or sequential) two-photon absorption where the second photon absorption takes place from a real level. (Fig. 2b). The difference in spectrometric (optical) properties is accompanied by a difference of other physical properties. The simultaneous process (a) has been successfully used for exciting photochromic molecules at specific positions inside a volume for 3D memory systems (writing process). A two-photon absorption process was also used to excite the written molecules that emit fluorescence (reading process) (Fig. 3) [17,18].

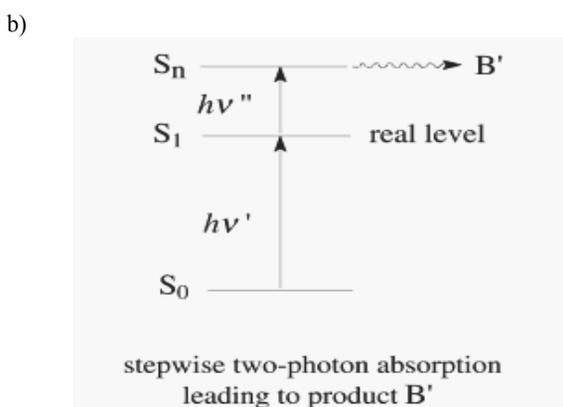
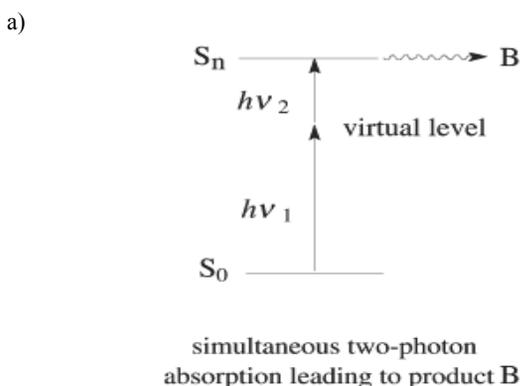


Fig. 2. Energetic levels in the tree-level system

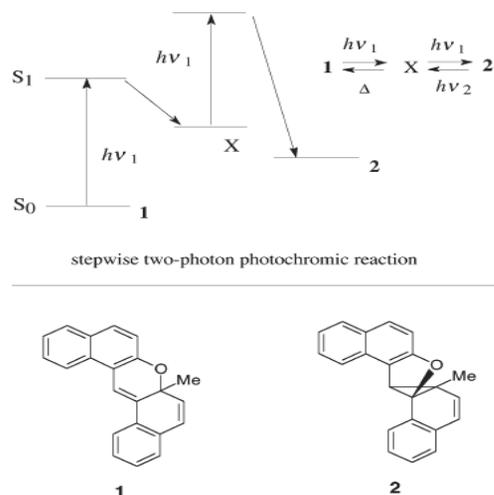


Fig. 3. Energetic levels for two-photon photochromic reaction

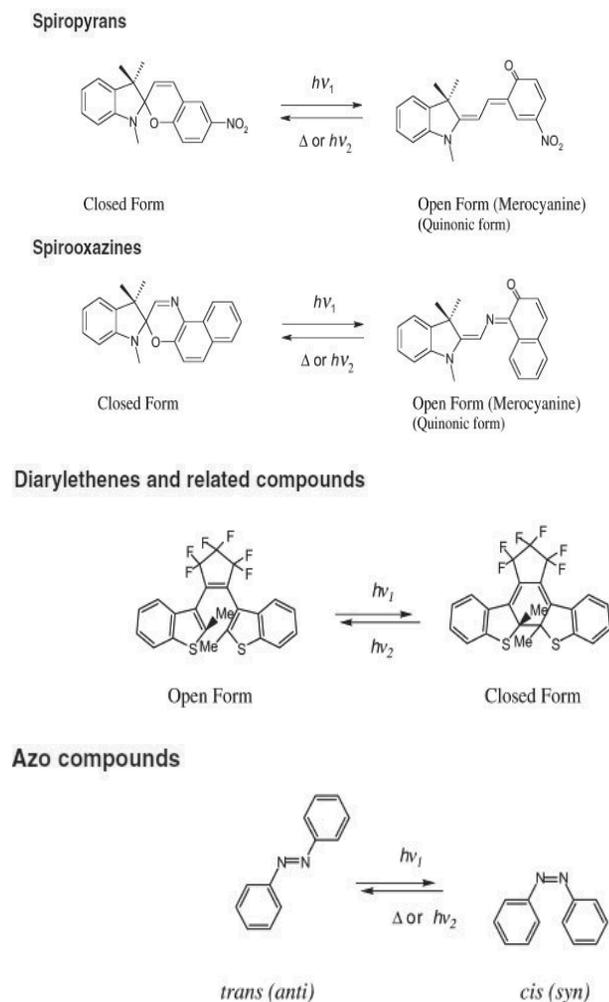


Fig. 4. Families of organic photochromic compounds

The excitation process can also proceed through a metastable intermediate (process b) as with the dinaphthopyran derivative (1). It was found to isomerize to the bicyclohexene derivative (2) via an intermediate X (not isolated). It has been used two 405-nm photons and observed that the quantum yield of 1→2 is proportional to the square of the photon irradiance. The reverse reaction 2→1 was found to proceed at 334 nm [19].

3.3. Families of organic photochromic compounds

Families of Spiroprans, Spirooxazines and Azo organic photochromic compounds are shown in Fig. 4. In all cases, $h\nu_2 < h\nu_1$.

4. Organic photochromic for three-dimensional memory

A photochromic compound is characterized by its ability to alternate between two different chemical forms having different absorption spectra, in response to irradiation by light of appropriate wave-memory media: (1) thermal stability of both isomers, (2) resistance to fatigue during cyclic write and erase processes, (3) fast response, (4) high sensitivity, and (5) nondestructive readout capability.

For 3D recording, a large two-photon absorption coefficient is preferred because 3D memory essentially uses a two-photon process to access a point within the volumetric medium. In the following section, typical photochromic compounds used for 3D memories will be described.

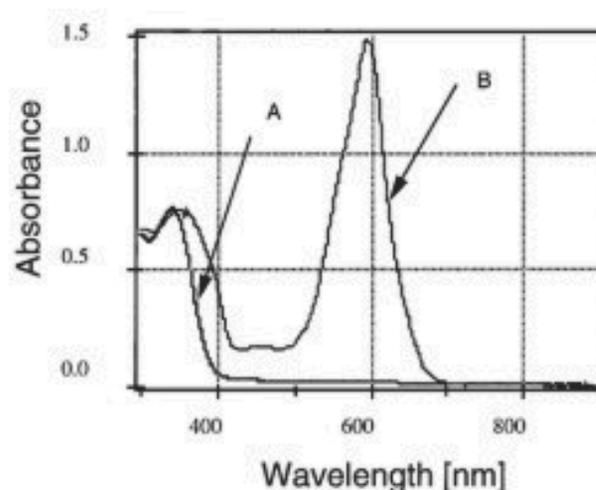


Fig. 5. Absorption spectra of a polystyrene film containing spiropbenzopyran both before (A) and after (B) exposure to 442-nm light

Spirobenzopyran Derivatives

Rentzepis et al. [20] first demonstrated a bit-oriented 3D optical memory system using a photochromic spirobenzopyran, the absorption spectrum of which is shown in Fig. 5. Isomer A has an absorption band shorter than 450 nm and, upon irradiation with ultraviolet (UV) light, it converts to isomer B, which has an absorption band around 600 nm (Fig. 5). Isomer B fluoresces around 700 nm upon photoexcitation with 500-700 nm light.

Figure 6 illustrates the principle of 3D optical memory based on a two-photon process proposed by Rentzepis et al. [20,21]. They used two beams to access a point in a volumetric recording medium. For writing data, which required excitation in the ultraviolet range, a two-photon absorption involving either a 1064 and a 532 nm photon (corresponding to 355 nm excitation) or two 532 nm photons (corresponding to 266 nm excitation). At the intersection of the two beams, isomer A absorbed two photons simultaneously and photoisomerized to isomer B.

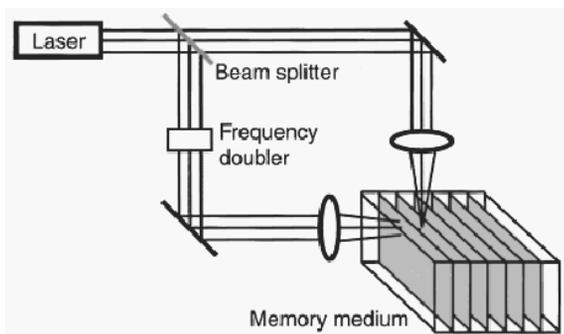


Fig. 6. Principle of 3D optical memories as proposed by Rentzepis et al. [20,21]

A similar two-photon process was employed for reading data. When isomer B molecules were excited by the absorption of two 1064 nm photons, the excitation caused only the written molecules to fluoresce. Although this fluorescence readout method is sensitive, the memory was erased during the reading process, due to partial used for occurrence of the reverse reaction from photoexcited isomer B to isomer A. Unfortunately, a destructive readout method such as this is not practical. The development of nondestructive readout methods is essential if this system is to become practical [8]. Thus, the most promising method is to read the memories by detecting the refractive-index changes that accompany the photoisomerization induced by long-wavelength light. This readout method does not induce photochromic reactions.

Nondestructive readout was demonstrated using a small difference in the refractive index of the spirobenzopyranisomers (Fig. 7) in the near-IR [22]. The small refractive-index change was detected using a near-IR laser-scan differential phase-contrast microscope (Fig. 7). The two isomers of the spirobenzopyran have very different absorption spectra, which suggests that the isomers also have different refractive indices. In the near-IR region around 800 nm, both isomers have negligible absorption. Therefore, the near-IR light needed to read the change of refractive index does not stimulate the photochromic photoreaction.

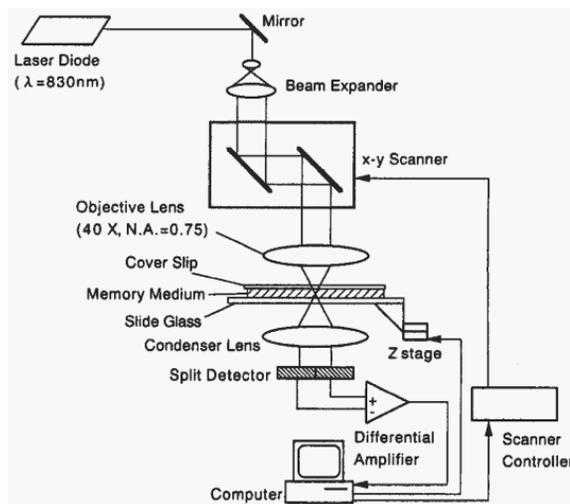


Fig. 7. Optical system for the readout of 3D memory. A near-IR differential phase-contrast microscope was nondestructive readout

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Data were recorded by focusing laser light (441.6 nm) on the two layers, which were separated by as much as 70 μm , using a laser scanning microscope as shown in Fig. 8. Bit sequences of 24 x 24 bits per layer which formed the letters "A" and "B" were obtained. The bit interval was 5 μm x 5 μm in each layer, and the separation distance between layers was 70 μm . Fig. 9 shows the readout from the two layers. The crosstalk between the layers was small enough to allow the recorded data to be clearly read by the differential phase-contrast microscope. Since the signal intensity was proportional to the derivative of the refractive index, the readings at the edges of the bits were slightly enhanced. The scanning rate was one layer per sec, and the readout could be repeated more than 7000 times without destroying the recorded information. The difference in the refractive indices of the two isomers was measured to be 0.02 nm at 830 nm. Unfortunately, the spirobenzopyrans used in the above system have poor durability and the photogenerated isomers were thermally unstable.

Diarylethene Derivatives

A diarylethene derivatives contain the heterocyclic rings, specifically (a) 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene and (b) 2-(1,2-dimethyl-3-indolyl)-3-(2,4,5-trimethyl-3-thienyl)maleic anhydride [8,23]. These compounds do not exhibit thermochromicity even at 200 $^{\circ}\text{C}$, and their colored, closed-ring forms are stable for more than 3 months

at 80 °C. Furthermore, the cyclization/ring-opening reaction cycle can be repeated more than 10^4 times without the loss of photochromic performance. Thus, diarylethene derivatives of this type currently are the most promising photochromic. 1,2-bis(2,4,5-trimethyl-3-thienyl)ethene (B1536) was used as a photochromic optical memory medium [24]. Unexcited B1536 exists as a yellow isomer that is converted into a red isomer upon irradiation with 380 nm light. The data written in this manner can be erased by irradiating the medium with 543 nm light.

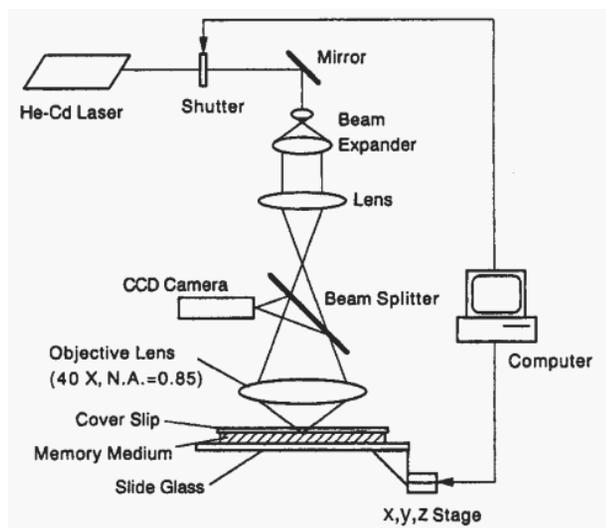


Fig. 8. Optical setup for recording 3D bit information in photochromic memory

This photochromic material (B1536) did not exhibit any apparent fatigue, even after 100 write/erase cycles. Furthermore, the written data (e.g. the red isomers) were stable at 80 °C for more than 3 months, and the thermal back-reaction (from the red isomer to the yellow isomer) did not occur, even at 200 °C. A two-photon process which focused on a point in the thick medium was used to record the data. A 760 nm Ti:sapphire laser operated in mode-locked pulsed laser mode was employed as the recording light source. Since the probability of two-photon absorption occurring is proportional to the squared intensity of the incident light, photoisomerization is only induced at the focal point, where the intensity is very high [20,25]. This technique is attractive for recording data in an erasable medium because it allows information to be written onto a particular layer without erasing the data already written on neighboring layers.

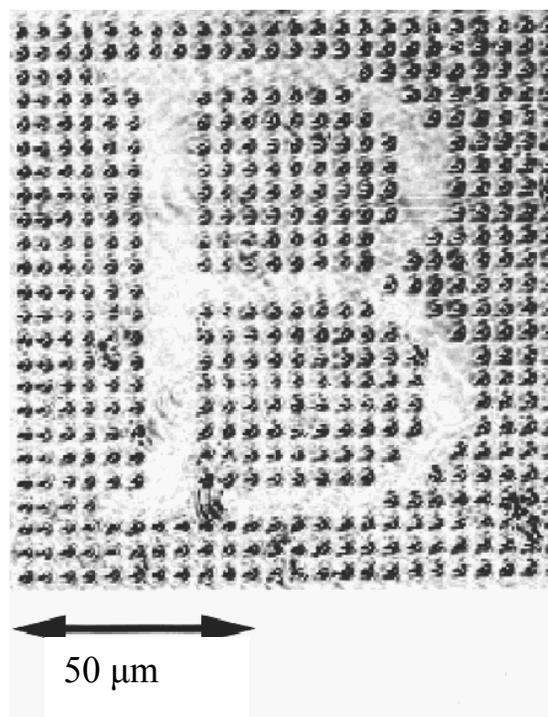
Figure 10 shows readout images of the bits written in 26 consecutive layers. The bit and layer intervals were 2 and 5 μm , respectively. The data were read using a reflection confocal microscope (RCM).

Azobenzene Derivatives

Azobenzene derivatives constitute a family of dye molecules which are well-known for their photochromic properties. These properties are due to reversible cis-trans photoisomerizations

which the derivatives undergo [26]. Azobenzene derivatives have two geometric isomers: a trans form and a cis form (Figure 5).

a)



b)

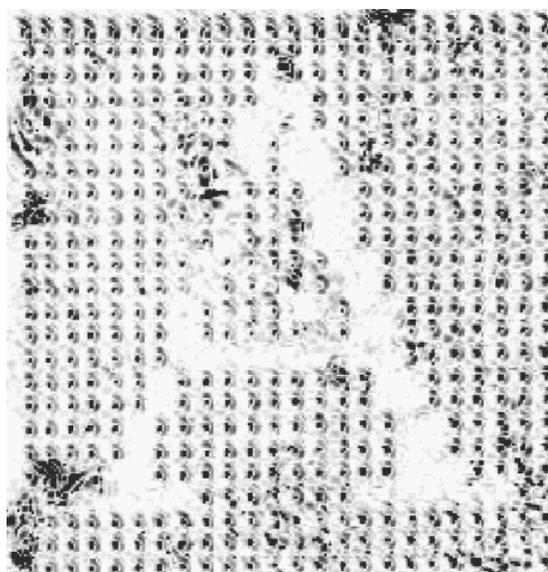


Fig. 9. Bit patterns read from photochromic memory using near-IR laser-scanning differential phase-contrast microscopy. (a) first layer, (b) second layer. The bit interval is 5 μm , and the layer distance is 70 μm [22]

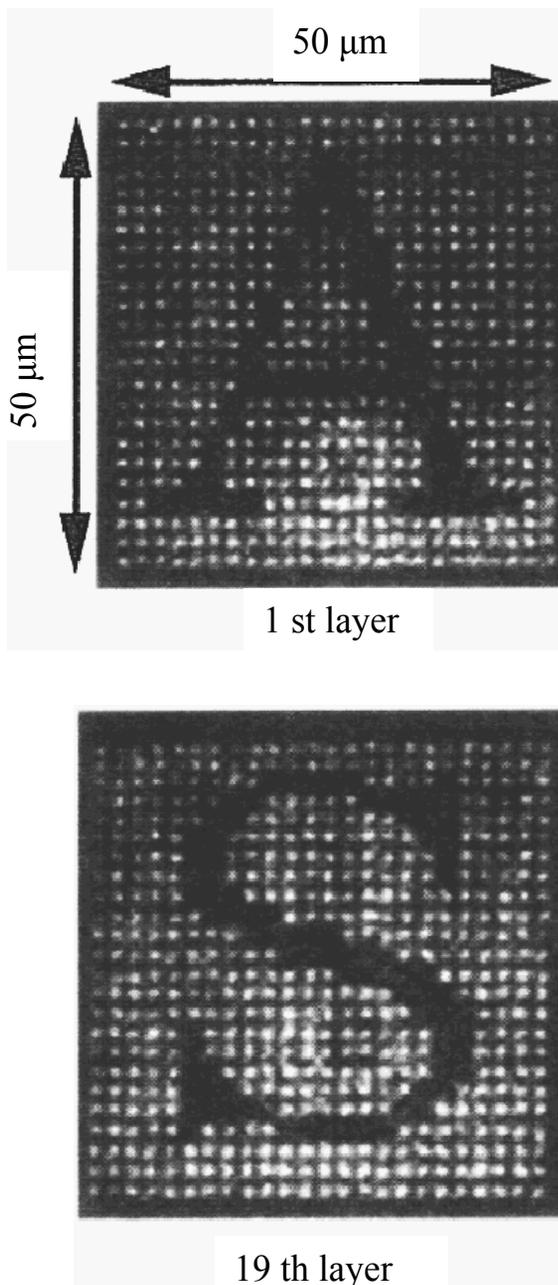


Fig. 10. Readouts of bit patterns written into photochromic memory using a diarylethene derivative. The data were read using a reflection confocal microscope [24]

The isomerization reaction that interconverts these two isomers may be light- or heat induced. The trans form is generally more stable than the cis form, thus the thermal isomerization usually occurs from the cis to the trans form. However, light induces transformations in both directions.

Another recording medium was developed by alternately coating photosensitive films (urethaneurea copolymer) and

nonphotosensitive films (poly-(vinyl alcohol), PVA) on a glass substrate. Fig. 11 shows the structure of the multilayered recording medium.

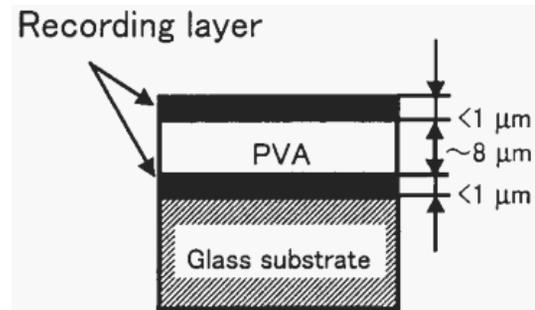


Fig. 11. Multilayered recording medium in which photosensitive films and nonphotosensitive transparent PVA films are alternately stacked

4.1. Single-Photon and Two-Photon Recording

Single-Photon Recording

Although two-photon excitation is the most desirable method for bit-data recording in 3D optical memories, single-photon recording also is an acceptable method since it gives good separation between the recorded planes. Fig. 9 show data recorded using a single-photon process. A typical system for single-photon recording is shown in Fig. 8. A He-Cd laser of 441.6 nm wavelength was used to record on the spirobezopyran medium, and an Ar⁺ laser of 488 nm was used to record on the urethaneurea copolymer medium. Crosstalk between the layers was negligible in the both cases.

Since single-photon recording does not require ultrashort-pulse lasers, conventional semiconductor lasers can be used. Thus, the optical systems utilized for recording in CD and MO devices can be readily applied to 3D optical memory recording.

Single-Beam, Two-Photon Recording

One reason of two-photon excitation is preferable for recording in 3D optical memory systems is because crosstalk between two adjacent layers is much reduced with this method. Another advantage of two-photon thermal excitation is that it reduces multiple scattering. This reduction occurs because the illumination beam that is utilized has an infrared wavelength. A typical optical recording system for single-beam, two-photon recording is similar to the one-photon recording system shown in Fig. 8, except that it uses a different light source. In the system shown in Fig. 8. A Ti:sapphire laser was used as the light source because this laser can provide the high peak power light which the cooperative nature of the two-photon excitation requires to produce efficient excitation. Other systems have been developed using a mode-locked Ti:sapphire laser [24,25,27] a mode-locked dye laser and a mode-locked YAG laser [26,28]. Continuous-wave light also has been investigated as a means of producing the two-photon process [29,30]. A high numerical-aperture lens is required to achieve separation of the layers, since this allows focusing on a well-confined spot at a point in a thick medium. The

disadvantage of ultrashort-pulse lasers is that they increase the cost of the recording device and make it difficult to produce a compact system.

Recently, a compact ultrashort-pulse laser in which an Er-doped fiber was used as the resonator was developed. Semiconductor lasers operated in mode-lock are also under investigation. Thus, the cost and the size of ultrashort-pulse lasers will decrease soon.

Right-Angle, Two-Beam, Two-Photon Recording

Rentzepis et al. have demonstrated a 3D memory device which uses two right-angle beams to access a point in a volumetric medium as shown in Fig. 6 [20]. This system clearly demonstrated that bit-oriented 3D memory storage can be achieved in this manner. Its disadvantages are that the two beams are difficult to align such that they intersect at the same point and that the working distance of the objective lenses are limited. Higher density storage was achieved using high NA objective lenses; however, the small working distances of the lenses still made it difficult to achieve the necessary right-angle configuration.

To solve these problems, Rentzepis et al. [21] proposed to use one beam as a plane addressing beam. The SHG light of a YAG laser was used for the addressing beam, while 1.06 μm wavelength light was used to carry the data. In this manner, they succeeded in recording 100 layers with intervals of 30 μm per layer and of 80 μm between layers.

5. Conclusions

Various optical systems for reading and writing 3D memories using photochromic materials were presented. The use of photochromic materials in 3D memory system is desirable because they present several major advantages over current optical systems, including their erasable/rewritable capability, high resolution, and high sensitivity. Several photochromic materials having adequate properties as 3D memory recording media were presented. The 3D recording techniques have been discussed which were described compliment, rather than conflict with, other techniques for achieving high-density memory storage, such as wavelength multiplexing, polarization multiplexing, and wavelength shortening. Combining these techniques results in increased storage density. Utilizing two-photon excitation is key to achieving effective 3D memory systems. Thus, photochromic materials with large two-photon absorption coefficients must be developed. The multilayered memory which defines 3D memory systems is just an extension of conventional optical memories into the z -direction, so the scanning, tracking, and auto-focusing techniques used in conventional memory systems can be adapted to work with 3D systems as well.

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